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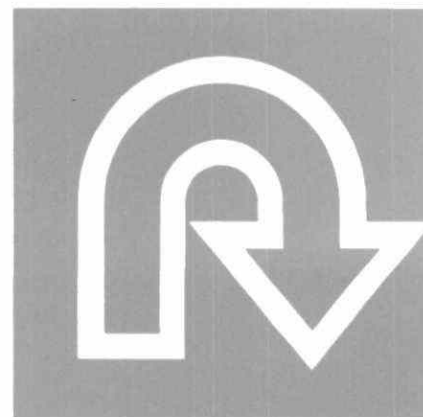
**ASSESSMENT OF THE STATE
OF KNOWLEDGE
ON THE LONG-RANGE
TRANSPORT
OF AIR POLLUTANTS
AND ACID DEPOSITION**

PART 6

**EFFECTS ON MAN-MADE
STRUCTURES**

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AUGUST 1986



ACIDRAIN

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Assessment of the state of
knowledge on the long-range
transport of air pollutants and
acid deposition.

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ERRATA

Assessment of the State of Knowledge on the Long-Range
Transport of Air Pollutants and Acid Deposition

Part 5, Human Health Effects

Page 5-5, paragraph 1

The third sentence should read as follows:

The incidence of colds going to the chest (38.3% vs 33.3%) and inhalant allergies (12.6% vs 5.1%) as identified from a questionnaire; cough with phlegm (10.0% vs 8.2%) and stuffy nose 25.3% vs 21.6%) as identified from a health diary were also higher in Tillsonburg than in Portage.

FEDERAL/PROVINCIAL RESEARCH AND
MONITORING COORDINATING COMMITTEE (RMCC)

ASSESSMENT OF THE STATE OF KNOWLEDGE
ON THE LONG-RANGE TRANSPORT
OF AIR POLLUTANTS AND ACID DEPOSITION

PART 6
EFFECTS ON MAN-MADE STRUCTURES

PREPARED BY P.J. SEREDA
FOR ENVIRONMENT CANADA

AUGUST 1986

ENTERED MAY 18 2001

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TABLE OF CONTENTS

	Page Number
6.1 INTRODUCTION	6-1
6.2 RECORDED EVIDENCE OF THE EFFECT OF ACID DEPOSITION ON BUILDING MATERIALS	6-1
6.2.1 Metals	6-1
6.2.1.1 Is There a Unique Value for "Corrosivity" of Each Site	6-2
6.2.2 Organics - Protective Coatings and Plastics	6-4
6.2.2.1 Are Any of Current Monitored Pollution Data Used in Rating Performance of Organics	6-4
6.2.3 Cementitious Materials - Stone, Brick Masonry and Concrete	6-5
6.3 MECHANISMS FOR ACID DEPOSITION EFFECTS ON MATERIALS	6-6
6.3.1 Metals	6-6
6.3.2 Cementitious Materials - Stone, Brick Masonry, and Concrete	6-6
6.3.2.1 Is Chemical Interaction of SO ₂ and NO _x the Main Mechanisms for Damage	6-7
6.3.2.2 Is There a Dose-Response Relationship	6-7
6.3.3 Is Acid Deposition a Single Cause of Deterioration	6-8
6.4 PREDICTABILITY OF EFFECTS OF ACID DEPOSITION ON MATERIALS IN STRUCTURES	6-9
6.4.1 Can Existing Test Data from Field Exposure of Metals be Used for Design Purposes	6-9
6.4.2 What is the Situation Regarding Prediction of Performance vis-à-vis Acid Deposition on Organic Materials	6-10

TABLE OF CONTENTS (continued)

		Page Number
6.4.3	What Records Exist of Pollution Data that Can Be Used to Evaluate Potential Damage to Materials	6-10
6.4.4	Can Existing Data on Pollution Be Used	6-14
6.4.5	Novel Method for Using Meteorological and Pollution Data for Predicting Performance of Materials	6-14
6.5	RECORDED EVIDENCE OF MATERIALS CORROSION AND DETERIORATION ON EXISTING STRUCTURES	6-15
6.5.1	Metals	6-15
6.5.1.1	Aluminium	6-15
6.5.1.2	Galvanized steel	6-15
6.5.1.3	Painted metals	6-15
6.5.1.4	Copper	6-15
6.5.2	Protective Coatings	6-16
6.5.3	Stone and Masonry	6-16
6.6	DAMAGE ASSESSMENT OF MAJOR ECONOMIC MATERIALS EXPOSED TO THE ENVIRONMENT AND THOSE AT RISK	6-17
6.6.1	Is Forecasting the Cost of Material Damage Possible	6-17
6.6.2	Inventory of Materials Exposed to the Environment	6-18
6.6.3	Consequences of Failure of Materials at Highest Levels of Risk	6-18
6.7	METHODS USED FOR MONITORING POLLUTION	6-19
6.7.1	Dry Deposition	6-19
6.7.1.1	What Method Can Be Used to Monitor Dose (Flux) Directly	6-19
6.7.1.2	IRMA Method	6-20
6.7.1.3	Analysis of Stone	6-20

TABLE OF CONTENTS (continued)

	Page Number
6.7.1.4 XPS Method	6-21
6.7.2 Wet Deposition	6-21
6.7.2.1 Wetting of Materials on Building by Rain	6-21
6.8 RESEARCH NEEDS	6-21
6.8.1 What Testing is Required	6-22
6.8.1.1 Recommendation for Monitoring the Distribution of the Time-Of-Wetness	6-22
6.8.1.2 Recommendation for Monitoring the Distribution of Pollutants Deposition Flux	6-22
6.8.1.3 Recommendation for Monitoring the Distribution of Chloride Deposition	6-23
6.8.2 Materials at Risk	6-23
6.8.2.1 What is the State of Materials on Buildings	6-24
6.9 ACKNOWLEDGEMENT	6-24
6.10 REFERENCES	6-24

EFFECTS OF "ACID RAIN" ON MAN-MADE STRUCTURES

6.1 INTRODUCTION

The final report of the Impact Assessment Work Group 1 (U.S. - Canada Memorandum of Intent on Transboundary Air Pollution) was issued on January 1983 and contained one section on "Effects on Man-Made Structures". This report is intended to serve as an update and a supplement to that Work Group 1 Report, and is in fulfillment of the contract with Atmospheric Environment Service dated 03 January, 1986.

Despite the voluminous literature on this subject area, there are specific sub-areas, where documentation is lacking, that will be discussed based on the author's considerable background experience in materials science and material performance.

In the context of this report "acid rain" or "acid deposition" includes: wet and dry deposition of SO_2 and NO_x and their secondary product including ozone and particles.

Finally, this report should be read in conjunction with the Work Group Report since it is intended primarily as an update to it.

6.2 RECORDED EVIDENCE OF THE EFFECT OF ACID DEPOSITION ON BUILDING MATERIALS

It should be noted at the outset that corrosion and deterioration of materials on man-made structures are common experiences and are due to many environmental factors involving many processes such as: freezing and thawing of masonry and concrete; efflorescence and salt crystallization spalling of brick; paint peeling, blistering and staining; corrosion of metals including reinforcing in concrete; and deterioration of roofing materials. Acid deposition with the resulting chemical and physical processes, may make a significant contribution to some or all of these processes. The value of Canadian construction in 1985 was \$61 billion (14% of the GNP). Repairs and maintenance were responsible for \$11 billion of the total construction costs. The question to be addressed in this report is: **what part of the observed corrosion and deterioration can be attributed to the effect of acid deposition?**

6.2.1 Metals

Atmospheric corrosion of steel, zinc, and copper has been studied extensively as documented in the Work Group 1 Report, giving considerable evidence that SO_2 dry deposition contributed to the corrosion. Various empirical relationships have been derived to fit the data collected by various exposure programs. These relationships

are no more than the correlations (best fit equations) of the measured microclimatic parameters and the observed metal loss in a given time. They do not explain the nature of the processes. All of the successful correlations include monitored values for the time-of-wetness or equivalent period of high humidity and SO_2 deposition velocity or sulphation rate. For coastal sites the correlations required a term to account for the chloride deposition. These studies have ignored any effect of NO_x , ozone or particular matter. These correlations also ignore any influence of physical processes involving the corrosion products or the surface characteristics. These factors, if they are functional, are reflected in the constants and indices. It should be noted that an extensive review of these factors is given by Brown and Masters (1982) where they discuss effect of temperature, chlorides, adsorption of water and the aspect of critical humidity in the presence of SO_2 . They also discuss the effects of NO_x and particulate matter.

6.2.1.1 Is There a Unique Value for "Corrosivity" of Each Site?

In the "50" and "60" decades there was a concerted effort made by ASTM Committees to quantify each exposure site for corrosion testing by a relative rating value where State College PA was given the rating of 1 (ASTM STP 435, 1968). Guttman (1982) lists 45 sites rated in increasing order of corrosion loss for steel in 2 year exposure, starting with Norman Wells, N.W.T., Can. being ranked 1st and Galeta Point Beach, Panama as 45th where the weight loss is 460 times higher than at Norman Wells. These data also give the ratio of steel/zinc weight loss, which varies from a low value of 9.8 to a high value of 364. Guttman (1982) in Table 6.1 gives ranking for 5 sites. The significance of this large variation was not appreciated fully.

TABLE 6.1 CORROSIVITY RANKING*

Site	Ranking		
	Fe	Cu	Zn
Cleveland	1	4	3
Ottawa	2	5	2
Trail	3	2	5
South Bend	4	3	4
Kure Beach 800	5	1	1

*Rankings are based on the average of 12-month exposure data (Guttman, 1982)

It was believed that monitoring of SO_2 dose, time-of-wetness and other pollutants such as chlorides, would allow characterization of the site corrosivity (Haynie, 1980; Knotkova et al. 1984).

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It was believed that monitoring of SO_2 dose, time-of-wetness and other pollutants such as chlorides, would allow characterization of the site corrosivity (Haynie, 1980; Knotkova et al. 1984).

National Research Council, Division of Building Research, at the advice of the Associate Committee on Corrosion Research and Prevention, undertook to establish "corrosivity" levels for 8 sites across the country during the period 1953 to 1966. It was the first testing agency to monitor the SO_2 deposition rate (sulphation method) during the corrosion test program. Results of this program were published by Gibbons (1970) which gives the relative "corrosivity" rating and the SO_2 deposition.

TABLE 6.2

Site	Corrosivity rating where Ottawa = 1 (based on 1 yr wt. loss of steel)	SO_2 deposition ($\text{mg SO}_3/100 \text{ cm}^2/\text{day}$) (ave. for period 1953-66)
Halifax (F.B.)	3.8	6.3
York Redoubt	1.5	0.28
Montreal	1.5	1.71
Trail	1.4	0.68
Ottawa	1.0	0.52
Saskatoon	0.6	0.16
Esquimalt	0.5	0.06
Norman Wells	0.03	0.01

It is obvious that there is a general correspondence of the "corrosivity" rating and the SO_2 deposition with the notable exception of the York Redoubt site. However, if this comparison was attempted for Zn or Cu the rating would be different as shown in Table 6.1. In the U.K., Shaw (1978) produced a Corrosion Map of the British Isles based on the exposure of zinc at 2195 sites, and SO_2 measured at 172 of these sites. A discussion of this data set is given by Saunders (1982). Haagenrud et al. (1983) give results of zinc and steel weight loss as a function of SO_2 at test sites in Scandinavia, that show reasonably linear plots over the range of approximately 10 to 18 $\mu\text{g}/\text{m}^3$.

Kucera (1983) in discussing the dose-response of various pollutants concluded that NO_2 in the range 0.05 to 0.5 ppm has no significant effect on the corrosion rate while SO_2 has a very strong effect. The most comprehensive experimental program designed to assess the relative damage function of pollutants is perhaps that now in progress (Flinn et al. 1985). Their results (Fig. 3, Flinn et al. 1985) indicate the large variation in the corrosion rates among the four exposure sites. The authors state that the twofold to sixfold range in the average corrosion rates for carbon steel, Cor-Ten A, copper and zinc indicate that there are substantial differences in the corrosivity of the atmosphere at the four sites. The authors also state that there is no simple relationship between these differences and any single environmental parameter. These observations lead them to suggest that the metals respond to the environments at the four sites in a unique way.

In the opinion of the author, the results of these numerous documented studies lead to the conclusion that there is a unique interaction between the microenvironment at the material surface and the material as defined by its physical and chemical characteristics, resulting in the observed corrosion. Therefore, the concept of the "corrosivity" of a site has no usefulness because it cannot be applied to a number of metals.

6.2.2 Organics - Protective Coatings and Plastics

Many papers report on studies of deterioration and weathering of paints, plastics, bituminous materials and sealants. Of these the most important in terms of dollar value is the group classed as protective coatings. Martin (1980) reviews this area and his work reflects the general view that U.V. irradiation along with humidity and temperature are the chief agents of deterioration and proposes a "solar weathering index" as a measure of the potential for deterioration at any given site. This paper is typical of most which address the rapid atmospheric weathering of organics without any consideration given to the possible influence of pollutants, both acidic deposition and ozone.

Sharman et al. (1983) report on weathering tests on sealants where cyclic movement is imposed in order to simulate the stressing factor that joints impose on sealants. This work is cited to emphasize the importance of the stress factor involved in the performance of these materials. It may be that the adhesive bond failure that this work shows for acrylic sealants as well as other sealants under stress may be due to both ozone and acid deposition but no specific measurements were made to verify such hypotheses. Ashton (1983) deals with tests that are used to evaluate performance and how important it is to simulate, and not exceed, the magnitude of certain key parameters when designing accelerated tests in contrast to the salt spray test for corrosion of coatings where the salt concentration is certainly excessive relative to most environments.

6.2.2.1 **Are Any of Current Monitored Pollution Data Used in Rating Performance of Organics?**

The Work Group 1 Report cites some work that gives dose-response relationships for erosion rate of oil base and vinyl base coatings due to SO_2 , but the results are strongly dependent on relative humidity and much less dependent on SO_2 concentration, especially in the case of the vinyl coatings. Funke and Haagen (1983) review the influence of SO_2 on organic coatings, and point out the remarkably high SO_2 permeability relative to other gases. They give the ratios of permeability of SO_2 relative to permeability of O_2 that range from 6.8 for polyethylene film, 15 for polycarbonate film and 65 for vinyl chloride copolymer film. Ranby and Rabek (1983) discuss environmental effects and give the main reactions. They conclude by stating that the problem of environmental corrosion of polymers is negligible in comparison with the physical, thermal and photochemical aging of polymers.

Although the NAPS collects data on Suspended Particulates (soiling index) and Total Suspended Particulates, which may influence the performance of coatings, at least in regard to appearance, there is no recorded observation to confirm or deny their significance. For materials on buildings and structures, the dynamics of rain water flow over the surface creates areas which are washed and areas which are not washed during rain storms resulting in dirt markings that affect the appearance and may require more frequent repainting. These effects are due to the combination of design features, amount of suspended particulates depositing on the surface and the nature of the surface material (Robinson and Baker, 1975). There is no documentation that attempts to quantify these parameters.

6.2.3 Cementitious Materials - Stone, Brick, Masonry and Concrete

Stone represents a very small portion of commercial construction materials and as such would rate little concern except that it was the main construction material for buildings now identified as cultural heritage and as such they must be preserved at all cost.

Deterioration of stone on historic buildings in Europe in the last 50 years presents positive evidence that pollution is responsible. Amoroso and Fassina (1983) show 3 photographs of the facade of St. Mark's Basilica in Venice, taken in 1900, 1930 and 1969. The first photo shows the sculpture four centuries old and in a good state of preservation. There appears little change in the 30 years between 1900 and 1930, but during the remaining 39 years the sculpture has eroded to the point that certain features, such as arms, have fallen off. Clearly there has been more deterioration in the last 40 years than in the previous four centuries. However, this deterioration cannot be represented in any terms of a damage function of pollution because deposition levels of SO_2 are not available.

Evidence of stone damage was collected by Baer and Berman (1983) by measurements made on 3909 marble tombstones in National Cemeteries. Various rates of erosion from 1.7 to 3.6 mm for 100 years life are given for the different sites and type of marble. However, these data cannot be used as evidence of pollution damage since no data for SO_2 or NO_x deposition are given.

Luckat, (1981) gives data for weight loss in percent for two sensitive stone samples, sandstone and limestone, when exposed to various concentrations of SO_2 . His data cover the SO_2 deposition range from 10 to 130 $\text{mg/m}^2/\text{d}$. The relationship given shows a greater rate of loss for sandstone than for limestone.

Several studies designed to provide dose-response relationships for marble damage by SO_2 and other pollutants, (Haynie, 1982, Livingston, 1981) had limited success because erosion of marble by water alone is significant and furthermore there is no single direct measurement (weight loss as in the case of metals) that represents the extent of

damage. In fact, marble or limestone samples exposed to environment with SO_2 but sheltered from the rain will gain mass while those exposed to the rain will lose mass (Weber, 1985). In either case damage can be internal as cracks in the microstructure and dissolution of binding material that will progressively result in failure that may be acting in combination with effects of cycles of freezing and thawing. This will be discussed in the section on mechanisms.

Brick masonry can be in the same class as stone with regard to historic buildings but it is mainly the mortar that can be seriously affected by pollution. SO_2 can contribute indirectly to efflorescence and salt crystallization which may be the main cause of ancient brick deterioration (Binda and Baronio, 1985).

Concrete is subject to the action of freezing-thawing, carbonation followed by reinforcing steel corrosion and the effect of de-icing salt in accelerating freezing-thawing and corrosion processes. There does not appear to be any direct evidence to link concrete deterioration with pollution. However, there is likewise no evidence to prove that pollution does not contribute to other processes of corrosion and deterioration.

6.3 MECHANISMS FOR ACID DEPOSITION EFFECTS ON MATERIALS

6.3.1 Metals

Although dose-response relationships for effects of acid deposition on the basic metals have been established, there is no clear understanding of the mechanisms involved.

6.3.2 Cementitious Materials - Stone, Brick, Masonry and Concrete

The common characteristic of this class of materials is their porosity. These systems are comprised of an assemblage of particles, crystals or agglomerates of various composition (microunits), cemented together at points of contact forming an interconnected pore system generally referred to as the microstructure. Thus gases and liquids from the environment can penetrate into the structure and be involved in chemical and physical interactions with the constituent materials. The size of the microunits determines the total surface area exposed to the environmental agents and in large measure determines the pore sizes and other physical characteristics. This class of materials represents a very broad range of physical and chemical characteristics and the recorded literature has not defined adequately the materials involved in the studies on effects of pollution in order to make valid comparisons. In this regard, the knowledge base of the materials science has not been fully employed to make the observations meaningful in terms of mechanisms of failure.

This class of materials is subject to a number of deterioration processes such as erosion by rainwater, freezing-thawing action, salt crystallization and spalling, as well as chemical interaction due to acidic deposition.

6.3.2.1 Is Chemical Interaction of SO_2 and NO_x the Main Mechanism for Damage?

It is generally agreed that SO_2 is the chief component of atmospheric pollution reacting with marble or limestone to produce gypsum. Amoroso and Fassina (1983) and Livingston and Baer (1983) discuss the various reactions that can take place when SO_2 enters the porous stone as a gas then is oxidized to sulphuric acid to react with calcite or even reacting as SO_2 gas to form CaSO_3 (Gauri and Gwinn, 1982). Many analyses have been carried out to show the presence of high concentrations of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) in the crust on stone and also inside the stone where gypsum is deposited in the pores, (Fassina, 1985, Luckat, 1981). Analysis of crusts, exfoliation and black deposits on stone confirm that SO_4^{2-} is the chief constituent and only trace amounts of NO_3^- are found leading to a tentative conclusion that NO_x is not contributing significantly to stone deterioration (Livingston, 1985, Fassina, 1985).

6.3.2.2 Is There a Dose-Response Relationship?

Several studies have attempted to show the relationship between SO_2 deposition and stone erosion without success for reasons already discussed in previous sections. One of the main reasons for lack of correlation must be the fact that deterioration of stone appears to be the greatest on areas of the structure that are exposed to high humidity and SO_2 pollution without being washed by rainwater. These areas develop scale or scab that exfoliates while areas that are washed by rainwater erode from the surface (Fassina, 1985). This observation poses the question whether dry deposition of SO_2 is the more destructive mechanism than wet deposition. It should be recognized that wet deposition may be a mixture of both dry deposition during dry periods followed by episodes of rain resulting in partial removal of accumulated acidic species by the rainwater combined with some deposition of acidic ions from the rain. Rainwater can wet the stone or other porous materials enabling both a dilution of ions present at the surface and the penetration of solutions into the pores by capillary action. When drying conditions follow there will be crystallization of certain salts such as gypsum inside the pores resulting in stresses.

Hicks (1982) discusses both wet and dry deposition, including the importance of such factors as condensation of water at a surface in increasing the velocity of deposition of small particles and gases. The fact that the surfaces of materials are often colder than ambient with resulting condensation may explain how surfaces can experience high acidic ion concentration during episodes of hoar-frost formation

(Ashton and Sereda, 1982). The above and other considerations pertaining to mechanisms of corrosion and deterioration lead to the conclusion that the most important parameter is the time-of-wetness. Clearly the presence of water is a common requirement for all the processes of deterioration and corrosion. Where chemical or electro-chemical processes are concerned the time-of-wetness is the reaction time.

6.3.3 Is Acid Deposition a Single Cause of Deterioration?

A level of corrosion and deterioration of all classes of materials would occur without any pollution and only the presence of water, oxygen, UV irradiation, climatic cycles of wetting and drying or freezing and thawing and biological agents. The question to be answered is what contribution does acid deposition make to the total deterioration. In the past, much work was focussed on trying to provide a dose-response relationship for one process from field studies where many processes of deterioration can occur at the same time thus making the initial objective virtually impossible. Laboratory studies where one process was studied at one time were equally limited because interpretation of results and their application to effects of multiple processes could not account for any synergistic action.

To illustrate the complexity of processes contributing to stone decay (which should be applicable to many porous materials), Tomback (1982) lists 5 major mechanisms and 20 sub-mechanisms that can be involved. The effect of each mechanism on the particular material depends on the chemical, mineralogical and physical characteristics of the material. For example, materials having a certain range of pore sizes are susceptible to freezing-thawing action. This is observed with brick where increasing the temperature of firing progressively renders the brick more resistant by virtue of the increasing size of pores. It is quite possible that acid deposition and the resulting chemical reactions producing new products can alter the pore structure and thus render a porous material more susceptible to frost action, but no recorded studies exist to verify this hypothesis.

Permeability of coatings to gases and liquids is a very important parameter in relation to its durability (Ashton, 1984). This property may be altered by the action of acid deposition which can serve to initiate or increase the action of other processes involved in deterioration. Coatings on metals provide protection of the metal surface by virtue of their low permeability to water, solutions and gases. If acid deposition should increase the permeability of coatings, then the protection against corrosion would be decreased. Again no recorded evidence exists to support this hypothesis. However, Funke and Haagen (1983) provide evidence that coatings like polymer films have a very high permeability to SO_2 relative to other gases such as O_2 and N_2 . This suggests that SO_2 may penetrate coatings on metals and undermine the interfacial bond.

This class of materials is subject to a number of deterioration processes such as erosion by rainwater, freezing-thawing action, salt crystallization and spalling, as well as chemical interaction due to acidic deposition.

6.3.2.1 Is Chemical Interaction of SO₂ and NO_x the Main Mechanism for Damage?

It is generally agreed that SO₂ is the chief component of atmospheric pollution reacting with marble or limestone to produce gypsum. Amoroso and Fassina (1983) and Livingston and Baer (1983) discuss the various reactions that can take place when SO₂ enters the porous stone as a gas then is oxidized to sulphuric acid to react with calcite or even reacting as SO₂ gas to form CaSO₃ (Gauri and Gwinn, 1982). Many analyses have been carried out to show the presence of high concentrations of CaSO₄·2H₂O (gypsum) in the crust on stone and also inside the stone where gypsum is deposited in the pores, (Fassina, 1985, Luckat, 1981). Analysis of crusts, exfoliation and black deposits on stone confirm that SO₄⁻² is the chief constituent and only trace amounts of NO₃⁻ are found leading to a tentative conclusion that NO_x is not contributing significantly to stone deterioration (Livingston, 1985, Fassina, 1985).

6.3.2.2 Is There a Dose-Response Relationship?

Several studies have attempted to show the relationship between SO₂ deposition and stone erosion without success for reasons already discussed in previous sections. One of the main reasons for lack of correlation must be the fact that deterioration of stone appears to be the greatest on areas of the structure that are exposed to high humidity and SO₂ pollution without being washed by rainwater. These areas develop scale or scab that exfoliates while areas that are washed by rainwater erode from the surface (Fassina, 1985). This observation poses the question whether dry deposition of SO₂ is the more destructive mechanism than wet deposition. It should be recognized that wet deposition may be a mixture of both dry deposition during dry periods followed by episodes of rain resulting in partial removal of accumulated acidic species by the rainwater combined with some deposition of acidic ions from the rain. Rainwater can wet the stone or other porous materials enabling both a dilution of ions present at the surface and the penetration of solutions into the pores by capillary action. When drying conditions follow there will be crystallization of certain salts such as gypsum inside the pores resulting in stresses.

Hicks (1982) discusses both wet and dry deposition, including the importance of such factors as condensation of water at a surface in increasing the velocity of deposition of small particles and gases. The fact that the surfaces of materials are often colder than ambient with resulting condensation may explain how surfaces can experience high acidic ion concentration during episodes of hoar-frost formation

(Ashton and Sereda, 1982). The above and other considerations pertaining to mechanisms of corrosion and deterioration lead to the conclusion that the most important parameter is the time-of-wetness. Clearly the presence of water is a common requirement for all the processes of deterioration and corrosion. Where chemical or electro-chemical processes are concerned the time-of-wetness is the reaction time.

6.3.3 Is Acid Deposition a Single Cause of Deterioration?

A level of corrosion and deterioration of all classes of materials would occur without any pollution and only the presence of water, oxygen, UV irradiation, climatic cycles of wetting and drying or freezing and thawing and biological agents. The question to be answered is what contribution does acid deposition make to the total deterioration. In the past, much work was focussed on trying to provide a dose-response relationship for one process from field studies where many processes of deterioration can occur at the same time thus making the initial objective virtually impossible. Laboratory studies where one process was studied at one time were equally limited because interpretation of results and their application to effects of multiple processes could not account for any synergistic action.

To illustrate the complexity of processes contributing to stone decay (which should be applicable to many porous materials), Tomback (1982) lists 5 major mechanisms and 20 sub-mechanisms that can be involved. The effect of each mechanism on the particular material depends on the chemical, mineralogical and physical characteristics of the material. For example, materials having a certain range of pore sizes are susceptible to freezing-thawing action. This is observed with brick where increasing the temperature of firing progressively renders the brick more resistant by virtue of the increasing size of pores. It is quite possible that acid deposition and the resulting chemical reactions producing new products can alter the pore structure and thus render a porous material more susceptible to frost action, but no recorded studies exist to verify this hypothesis.

Permeability of coatings to gases and liquids is a very important parameter in relation to its durability (Ashton, 1984). This property may be altered by the action of acid deposition which can serve to initiate or increase the action of other processes involved in deterioration. Coatings on metals provide protection of the metal surface by virtue of their low permeability to water, solutions and gases. If acid deposition should increase the permeability of coatings, then the protection against corrosion would be decreased. Again no recorded evidence exists to support this hypothesis. However, Funke and Haagen (1983) provide evidence that coatings like polymer films have a very high permeability to SO_2 relative to other gases such as O_2 and N_2 . This suggests that SO_2 may penetrate coatings on metals and undermine the interfacial bond.

6.4 PREDICTABILITY OF EFFECTS OF ACID DEPOSITION ON MATERIALS IN STRUCTURES

The ultimate objective of all testing and evaluation of materials is the prediction of their performance in service.

6.4.1 Can Existing Test Data from Field Exposure of Metals be Used for Design Purposes?

The limitations of the massive existing test data have been discussed in section 6.2. However, some guidance can be derived from the existing correlations provided that the time-of-wetness can be estimated. Not only must the climatic variations, as discussed by Ashton and Sereda (1982), be taken into account but in addition the location on the structure must be considered. Sereda et al. (1980) showed that specimens of metal exposed at an angle of 30° to the horizontal on a clear night will be 2 to 4°C colder than ambient, and plastic specimens will be 4 to 6°C colder than ambient, resulting in condensation as dew or hoar-frost and detected as moisture when the ambient RH was as low as 80%. This work showed that the condition when the surface temperature is lower than ambient contributes 70 to 96% of the time-of-wetness. By actual measurement of the time-of-wetness due to condensation, Yamasaki (1983) showed that on the average, condensation contributes 64.6% of the time-of-wetness (twice that due to precipitation) for surfaces exposed at 30° to horizontal and facing south. Yamasaki (1984) also showed that changing the exposure angle from horizontal to vertical results in large changes in surface temperature for the same ambient conditions with a corresponding change in the yearly mean time-of-wetness from 35% for horizontal surfaces to 21% for vertical surface.

The above observations indicate that large variations in the time-of-wetness are to be expected for surfaces exposed at various locations on a building depending on design, height, direction of exposure, etc. This was verified in one study by Guttman (1982) as shown in Table 6.3 where 3-fold variation had been recorded between the wall and roof overhang exposures.

TABLE 6.3 Percentage time-of-wetness on galvanized sheet metal exterior walls and roof of a storage building, Trail, B.C. (data collected by Guttman, see Sereda, 1974, reference 20)

West Exposure		South Exposure		North Exposure		
Wall (midheight)	Roof (overhang)	Wall (near roof overhang)	Wall (midheight)	Roof (overhang)	Wall (near roof overhang)	Wall (midheight)
23.6	50.3	14.6	18.5	51.1	23.2	21.1

It is common experience that materials near and at the top of a building deteriorate more than similar materials on lower levels. This is a reflection of the increased time-of-wetness not only due to wetting by rain but also increased condensation as found by Sereda (1974) in measuring the time-of-wetness in the cavity of walls in a three-storey building where the yearly mean value for the top location was 38% and the bottom location was 26%.

The second major parameter that must be determined in order to make any prediction about effects on materials on structures is the rate of acidic deposition. It has already been mentioned that there is a problem when considering the contribution of dry and wet deposition. Furthermore, the dry deposition is determined from the concentration of pollutant in the air and the deposition velocity. As far as materials on structures are concerned, the concentration values are available only for ground level and no measured values are available to indicate the variation of concentration with height. Many local sources are chimneys at the top of the building so that it is quite likely that SO_2 concentration may be much higher at the top of tall buildings. Likewise the deposition velocity can vary greatly depending on size of particles or gas, the nature of the surface including condensing conditions, orientation of surface whether horizontal or vertical, values given range from .02 to 2.5 cm s^{-1} (Davies and Nicholson, 1982; Hicks, 1982; Nriagu, 1978; Judeikis and Stewart, 1976). Finally it can be expected that particulate matter will be present at a higher concentration in the heart of a city than in the outskirts or rural areas (NAPS, 1984). The mean value for the station in the botanical gardens in Montreal was less than half of the value for a station at a nearby busy intersection at Duncan and Decarie ($40/106 \text{ g/m}^3$). Particulate matter can accelerate corrosion or surface deterioration (Nriagu, 1978; Kucera, 1978) in the presence of gaseous pollutants. Clearly what is required is the time-of-wetness and the rate of deposition of SO_2 , NO_x and particulate matter for each material component of a building. If such data were available, a reasonable estimate of the severity of exposure could be charted for materials in a building.

6.4.2. What is the Situation Regarding Prediction of Performance vis-à-vis Acid Deposition on Organic Materials?

What has been said above regarding metals is also applicable to the organics except that there is the additional need to monitor the total UV irradiation on different parts of a building and it is also useful to have the number of wetting-drying cycles as has been measured by Yamasaki, (1984).

6.4.3 What Records Exist of Pollution Data that Can Be Used to Evaluate Potential Damage to Materials?

As early as 1953, NRC/DBR began monitoring sulphation rate at eight exposure sites across Canada (Gibbons, 1970) located at Esquimalt,

Norman Wells, Trail, Saskatoon, Ottawa, Montreal, Halifax (F.B.) and York Redoubt. The Montreal and Halifax (F.B.) sites were located downtown on the roofs of buildings and were probably quite representative of the highest levels of SO_2 . The sulphation rate average for ten years was ten times higher on the roof site in Halifax than that at Ottawa (see Table 6.2) due to the close proximity of a stack and the burning of high sulfur coal. The rate of corrosion was equally severe, galvanizing on steel (2 oz/sq. ft.) was completely corroded in a period of 44 months.

Monitoring has been continued to the present time at Saskatoon, Ottawa and Halifax (roof of Atlantic Regional Laboratory, ARL) and the data given in Table 6.4 show the decreasing trend in SO_2 deposition for the Ottawa and Halifax sites although the values for Saskatoon site for those particular years appear to have the opposite trend.

TABLE 6.4 Yearly average values of SO_2 deposition rate ($\text{mgSO}_3/100 \text{ cm}^2/\text{d}$)

	1964	1974	1984
Ottawa	0.62	0.40	0.20
ARL*	0.66	1.13	0.33
Saskatoon	0.08	0.24	0.30

*Atlantic Regional Laboratory, NRC

The monitoring by NRC showed a consistent yearly cycle having highest sulphation rates in the winter months and lowest values in the summer. Table 6.5 shows an extreme case from the Halifax site.

TABLE 6.5 Atmospheric Sulphur Dioxide on roof of federal building, Halifax, 1955 ($\text{mg SO}_3/100 \text{ cm}^2/\text{day}$)

Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
22.7	18.4	21.8	14.8	14.8	4.4	1.5	1.5	10.5	15.4	18.7	27.6

For Ottawa site the monthly average values for the ten year period 1970-79 varied 3 fold from winter to summer. McKenzie and Vassie (1985) give similar seasonal variation of 2 to 4 fold in the U.K. Amaroso and Fassina (1983) give values for SO_2 in Venice obtained in 1972 of $370 \mu\text{g}/\text{m}^3$ in February and $18 \mu\text{g}/\text{m}^3$ in June.

In Canada as pollution abatement legislation of local and provincial governments took effect during the early 1970's, variation in urban sulphation rate between winter and summer began to decrease (see Table 6.6(a) & (b)). It is reasonable to conclude that the summer values represent the "background" SO_2 level mostly due to long range transported pollution while the winter values represent the contribution of the local sources to the "background".

TABLE 6.6(a) NAPS Data 1974

Station	J	F	M	A	M	J	J	A	S	O	N	D
Charlottetown	2.4	1.9	0.5	0.5	0.5	-	-	-	0.5	1.2	1.6	1.1
Halifax (30101C)	5.6	5.2	4.1	2.9	2.1	1.6	1.7	1.7	1.1	-	-	-
St. John (40202C)	4.0	4.6	-	1.8	2.3	1.8	2.0	1.0	1.0	2.2	1.0	0.9
Quebec City (50304C)	-	-	-	-	-	-	1.9	2.4	-	0.8	5.3	-
Montreal (50102R)	1.1	2.8	2.2	2.4	1.9	1.4	1.1	0.5	0.6	0.9	0.5	0.4
Montreal (50105C)	8.9	11.9	7.8	6.7	2.9	1.0	-	-	1.0	4.3	6.3	7.4
Ottawa (60101C)	4.9	6.3	4.6	2.3	1.1	0.3	0.4	0.3	0.4	1.7	2.2	3.4
Toronto (60402R)	2.0	1.5	1.3	1.5	1.3	2.1	1.6	1.8	1.2	2.7	2.5	1.5
Toronto (60411R)	1.0	.9	1.1	1.1	0.9	1.1	0.6	0.6	0.3	0.2	0.4	0.6
Hamilton (60501C)	2.0	3.3	2.3	2.1	2.7	2.0	1.3	1.5	1.3	2.8	1.9	2.6
Winnipeg (70101C)	0.1	1.3	1.4	0.1	0.0	0.0	-	0.1	0.1	0.1	0.1	0.9
Saskatoon	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Regina	0.0	0.0	0.0	0.0	0.0	-	0.0	0.0	0.0	-	0.0	0.0
Calgary (90220R)	0.5	0.4	0.2	0.1	0.1	0.1	-	0.1	0.1	0.1	0.0	0.0
Edmonton (901211)	0.1	0.1	0.0	0.0	0.0	0.1	0.0	0.1	0.2	0.1	0.1	0.1
Vancouver (00105C)	0.6	0.6	0.7	1.0	0.5	0.5	-	1.1	0.6	0.6	0.3	0.4

*Values in parts per 100 million

TABLE 6.6(b) NAPS DATA 1984

Station	J	F	M	A	M	J	J	A	S	O	N	D
Charlottetown	1.1	xx	xx	1.1	xx	xx	xx	-	-	xx	xx	-
Halifax (30116C)	-	1.6	1.5	-	1.1	1.2	xx (0.6)	-	-	1.1	1.3	-
St. John (40202C)	1.3	xx	xx	3.8	1.2	-	-	xx	xx	xx	xx	xx
Quebec City (503031)	1.3	2.8	3.0	4.8	2.6	3.2	1.0	2.6	xx	1.4	1.3	1.1
Montreal (50102R)	2.5 (2.)	1.8	1.3	xx (1.0)	xx (0.5)	xx (0.5)	-	xx (0.5)	xx (0.8)	1.7	1.2	1.4
Montreal (50110C)	1.7	1.8	1.2	xx (0.8)	1.0	1.3	xx	xx (0.5)	xx (0.3)	-	xx (0.6)	xx (0.8)
Ottawa (60101C)	xx	1.7	1.2	1.2	1.4	1.1	xx	xx	xx	xx	xx	-
Toronto (60402R)	1.9	1.3	xx	xx	xx	xx (0.7)	xx	xx	xx	xx	xx	xx (0.9)
Toronto (60412R)	1.7	1.4	xx (0.3)	xx (0.5)	xx (0.5)	xx (0.6)	xx (0.6)	1.1	xx (0.)	xx (0.7)	1.1	xx (1.0)
Hamilton (60501C)	1.9	1.7	1.6	2.2	1.3	1.3	xx	1.3	1.1	2.0	xx	1.2
Winnipeg (70118R)	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx
Saskatoon	xx	-	-	xx	xx	xx	xx	xx	xx	xx	-	xx
Regina	xx	xx	-	-	xx	xx	xx	xx	xx	xx	xx	xx
Calgary	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx (0.1)	xx	xx (0.3)
Edmonton	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx
Vancouver (00110R)	-	1.0	xx (0.7)	xx (0.4)	xx (0.3)	xx (0.5)	xx (0.5)	xx (0.3)	xx	xx (0.6)	xx (0.3)	xx (0.4)

xx - below 10 ppb

Values in parts per 100 million

Values in () were supplied from raw data not published at present

For a number of years, the Ontario Department of Energy and Resources Management monitored sulphation rates at 46 stations in Metro Toronto. Data collected were published by Sereda (1974) showing a dramatic decline in sulphation rates in the 5 years between 1967 and 1972, going from levels of about 3.0 to 0.5 mg SO₃/100 cm²/day for the downtown areas. All values were obtained at ground level. Monitoring has been discontinued.

Since the early seventies, there has been a National Air Pollution Surveillance (NAPS) program monitoring SO₂ concentrations at 77 urban stations at ground level. Additional stations are operated by provincial agencies in various locations but all these involve automated apparatus giving concentrations of SO₂ and only in a few instances are sulphation plates used. Therefore, comparisons with earlier data obtained in Toronto and at sites operated by NRC, are not possible. Furthermore, many of the values are below 10 ppb and are not reported, thus the annual mean values for 1984 are not given for most locations (NAPS, 1984). Comparison of Table 6.6(a) and (b) shows a significant decline in SO₂ levels in all the cities where monitoring is carried out in the 10 year period.

It should be noted that the SO₂ concentrations given by Flinn et al. (1985) for the five sites operated in the U.S.A. by NAPAP range from 3 to 21 ppb (annual mean) and are not too different from those in Canada.

6.4.4 Can Existing Data on Pollution be Used?

The conclusion given in section 6.2.1.1 dealing with the "corrosivity" of sites can now be reinforced with the evidence presented in subsequent sections. Clearly the compiled data on concentrations of SO₂, NO_x, particulate matter and ozone could not by itself indicate the severity of corrosion or deterioration of materials. This is confirmed by Flinn et al. (1985) when they state the following:

"The twofold to sixfold range in the average corrosion rates for carbon steel, Cor-Ten A, copper and zinc indicate that there are substantial differences in the corrosivity of the atmospheres at the four sites. There is no simple relationship between these differences and any single environmental parameter listed in Tables 4-7. There apparently is a factor or combination of factors, characteristic of the Washington D.C. site that serves to inhibit the corrosion of copper. This factor or combination of factors does not have the same effect on the corrosion of Cor-Ten A".

6.4.5 Novel Method for using Meteorological and Pollution Data for Predicting Performance of Materials

Rychtera, (1985) proposes a novel approach to the problem of evaluating and predicting deterioration of technological materials when exposed to various environmental conditions. The environmental conditions of

temperature, relative humidity, pollution and their interaction with the materials are combined as a series of stress factors; sorption stress, temperature stress, corrosion stress and microbiological stress. The unit of stress is one day. The assumption made is that for a given level of the real stress and time interval, there is a corresponding time interval for a test under model conditions resulting in the same degradation change. The author classifies the materials into eleven classes, the materials in each class are considered to have similar stress characteristics. It would be surprising if this simplified approach was to provide useful guidelines for predicting performance because it does not take into account microclimatic conditions and does not include such deteriorating factors as ultra violet irradiation.

6.5 RECORDED EVIDENCE OF MATERIALS CORROSION AND DETERIORATION ON EXISTING STRUCTURES

6.5.1 Metals

Documentation of case histories involving corrosion of metals on buildings is scarce, although many cases exist from personal observations.

6.5.1.1 Aluminium

Kucera (1978) presents evidence of corrosion of anodized aluminium cladding on buildings in areas sheltered from the rain. He recommends that such areas be washed at regular intervals. This is evidence of how design influences performance of materials in structures.

6.5.1.2 Galvanized Steel

Galvanized steel fencing, which is found in urban and rural locations, can serve as a good indicator of the severity of the environment in different localities. A survey of the service life of a given type of fencing (chain link security) would be useful to provide a rough index of acid deposition effects (Stankunas et al. 1982).

6.5.1.3 Painted Metals

Corrosion of painted autobodies has been a serious concern for many years. It is suggested that acid deposition is contributing to the corrosion (Baboin, 1986) but this effect is masked by the more serious effect of de-icing salts. The latter evidence may be relevant to deterioration of paint in coastal areas.

6.5.1.4 Copper

Copper on the roofs of the Parliament buildings in Ottawa, as in other places, represents a special aesthetic quality after it is covered by

the green patina due to a certain type and amount of corrosion. Prior to the closing of a paper mill immediately on the opposite side of the Ottawa River in 1972, copper developed good patina in about 10 years exposure on Parliament Hill. Since the closing of this mill, the patina does not want to form and Public Works Department is forced to apply artificial "patina" coatings on new copper in order to match the appearance of the old copper. This is one instance that local pollution served some purpose. The writer's own house has copper flashing which began to show the characteristic patina after about 25 years of life in Ottawa in a residential area.

6.5.2 Protective Coatings

As discussed in previous sections of this report, "weathering" of paints is relatively rapid and service life correspondingly short so that no effort has been made to identify the contribution of acid deposition to the overall deterioration.

6.5.3 Stone and Masonry

Most of the case studies of deterioration of marble and limestone involves historic buildings in Europe. Weaver (1985) has reported on acid deposition effects on stone of the Parliament Buildings in Ottawa.

Amoroso and Fassina (1983) describe marble deterioration in St. Marks Basilica in Venice and in a number of other buildings. Much documentation is provided to support the observations, including properties of the stone and environmental parameters such as concentration of pollutants.

Garbassi and Mello (1985) report on a study of marble sulphation on Colonna Antonina, Piazza Colonna, Rome. They used in-situ XPS to observe first stages of sulphation and monitored SO_2 and NO_x concentrations at elevation of 4 m and 30 m. This is a very important contribution to the understanding of acid deposition on marble deterioration.

Fassina, (1985) reports on a study of stone deterioration on Loggia Cornaro in Padova giving extensive analyses of crusts, exfoliations and surface deposits which indicate the possible contribution of various components of pollution.

Livingston (1985) provides a compilation of analyses of stone from various localities to show the relative concentrations of products from reactions with SO_2 and NO_x . The ratios of SO_4/NO_3 range from 0.6 to 1600. Most values are high to indicate the predominance of SO_4 in stone taken from buildings. Other cases are reported by Keppens et al (1985), Winkler (1985), Webber (1985), and Skoulikidis et al. (1981).

6.6 DAMAGE ASSESSMENT OF MAJOR ECONOMIC MATERIALS EXPOSED TO THE ENVIRONMENT AND THOSE AT RISK

It is suggested that a rough estimate of materials loss due to all causes of deterioration and corrosion can be obtained from records of yearly value of different classes of materials, their relative exposed areas on structures and an estimate of the damage function. Clearly the most difficult value to estimate is the damage function. However, the relative dollar values of the different classes of materials indicates that one need to consider only several classes of materials, namely; protective coatings, brick masonry, bituminous roofing and concrete being significant. For the present, concrete can be omitted because the general opinion is that acid deposition is not likely to play a significant role in the deterioration process.

This major question of estimating the economic impact of acid deposition on materials has been studied extensively in 1984-85 by Brookhaven National Laboratories, E.P.A. Mathtech Inc., sponsored by Department of Energy and National Parks Service. Most of the derived information has been compiled as internal reports and in some cases, as papers submitted for publication and as such is not possible to document properly in this report. Therefore, reference to the above work will be made in general terms except in a few cases.

The approach taken by all these recent studies involves an assessment of the damage function for the class of material, an inventory of materials exposed on the housing and building stock, and a unit maintenance replacement cost. For such analyses many assumptions must be made that are not verified by field surveys and studies on individual buildings.

It is not certain that the sophisticated approach reflected in the recent studies is justified when paint is estimated to represent more than 50% of the total loss, for which the damage function is poorly defined. The other class of materials representing significant loss is brick masonry for which the damage function is likewise poorly defined.

6.6.1 Is Forecasting the Cost of Material Damage Possible?

A number of recent reports (Wyzga and Lipfert, 1985, Haynie, 1985; Lipfert et al. 1985) address the above question. These and a series of internal reports by the agencies mentioned in 6.6, examine the validity and errors involved in the derivation of damage functions for a number of materials. These reports discuss the factors of atmospheric variability, effects of scale, effects of configuration, and the

interaction between pollutants and atmospheric conditions. This was done in order to assess the applicability of the results of controlled laboratory and field experiments to conditions in the real world, from which the economic assessment of corrosion damage could be made. The uncertainties of estimating the effects of air pollution is dealt with by Stankunas et al. (1982), using the case of chain-link fence cost of maintenance analysis, including various strategies for maintenance. This paper clearly shows the serious limitations in such analysis even in the case of corrosion of zinc for which the damage function has been well established.

This short report cannot undertake to review the above extensive series of reports. It is noted, however, that various assumptions were made regarding variability in deposition velocity based on the theory of air flow and wind velocity profiles etc., but these were not confirmed by any measurements on actual structures. The same can be said regarding distribution of SO_2 concentration with height and the distribution of the time-of-wetness on materials in a structure as discussed in several sections in this report. There is no account taken of the rain wetting profiles on building which are involved in "wet" deposition as well as having a major influence on staining due to the uneven washing by rainwater of surfaces with deposits of particulate matter. Rain washing of stone has a major influence on the type and severity of effects of dry deposition as discussed in other sections of this report.

6.6.2 Inventory of Materials Exposed to the Environment

Inventories of various classes of materials on various types of housing and non-residential buildings have been assembled from data bases and from field sampling such as that done by Merry and LaPotin (1985). These show the predominance of bituminous roofing, painted surfaces, brick masonry surfaces and concrete with minor percentages of other classes such as bare metals, stone, glass and plastics. Whereas these inventories are necessary to provide the overall assessment, it should be remembered that the contribution to the overall economic loss of the minor classes is small and do not justify a precise accounting. It may be adequate to determine the inventory from statistics of the market use of the different classes of materials. What is important, however, is to recognize that not all the material of a given class on a building is at the same level of risk. Paint on a horizontal surface and near the top of a building is at a higher level of risk than the paint on the vertical surfaces near the bottom of a building. This is discussed in other sections of this report.

6.6.3 Consequences of Failure of Materials at Highest Levels of Risk

If a wall is painted and one portion (because of its location and consequent severe exposure) fails, then the whole wall may need to be repainted. It is this aspect that suggests that damage functions may need to reflect the worst case rather than the average. In this regard

the influence of design can be very great. Furthermore, a premature failure of a minor constituent such as flashing or sealant can result in a failure of a major constituent such as a masonry wall after it becomes saturated with rain leaking into the structure. Such cases have occurred often in the experience of the author.

6.7 METHODS USED FOR MONITORING POLLUTION

Most pollution data currently available, give values of concentration of SO_2 , NO_x and ozone in ppb, pphm or $\mu\text{g}/\text{m}^3$. Total suspended particulate matter are given in $\mu\text{g}/\text{m}^3$ (National Air Pollution Surveillance, Environment Canada, EPS7/AP/16, 1985).

6.7.1 Dry Deposition

From the review of the literature as discussed in this report, dry deposition of gaseous pollutants is the mode of delivery that is of importance in assessing damage to materials in structures. Therefore, the parameter that is significant is the rate of deposition (flux or dose) on the surface of a given material, derived from concentration values and velocity of deposition (Haynie, 1980, 1983; Amoroso and Fassina, 1983; Nriagu, 1978; Hicks, 1982).

The velocity of deposition depends on the nature of the material, relative humidity of the air, roughness of the surface and wind velocity and season (atmospheric stability) as discussed by Nriagu (1978), Livingston and Baer (1983), and Haynie (1980). If the pollutant is in aerosol state or different sized particulate matter, then the deposition velocity is a complex function of size, orientation of the surface etc. as discussed by Amoroso and Fassina (1983).

Since much of the current data base gives pollution levels of SO_2 , NO_x and ozone as concentration in ppb or as $\mu\text{g}/\text{m}^3$, there is need to estimate the velocity of deposition to obtain values of flux.

6.7.1.1 What Method Can be Used to Monitor Dose (Flux) Directly?

Perhaps the passive monitors referred to as sulphation and nitration plates (Huey, 1968) come the closest to provide a value of the rate of acidic deposition on the surface given in $\text{mg SO}_3/100 \text{ cm}^2/\text{day}$. It is a standard method of ASTM (1985) and has been used by NRC (Gibbons 1970). This method has been used in U.K. where it was first developed, (McKenzie and Nassie, 1985). This method involves the collection of SO_2 on a lead peroxide coated surface and NO_x on the triethanolamine coated surface. In Europe a similar method is used involving the collection of SO_2 on sodium carbonate coated pulp filter (Liesegang method) as was used in a study by Knotkova et al. (1984).

The sulphation and nitration method is very sensitive to wind speed and relative humidity so that the CF (calibration factor) was found to increase by a factor of 3.1 for sulphation plates and 4.5 for nitration plates when wind speed was reduced from 4.7 to 0.7 ms⁻¹, (Sickles and Michie 1986). Of course this affects only the conversion of the flux values to concentration of gas in the air stream. The value that is most useful for assessing material damage is the flux and it is reasonable to assume that the material surfaces will respond to changes in humidity and wind velocity in a similar manner to the sulphation or nitration plate surface. The reactivity, however, will be greater on sulphation and nitration plates than on other materials. One could conclude that the flux recorded by these plates will be higher than the flux on material surfaces but the extent of the difference is not known. However, it can be argued that the relative values of the flux (monitored by sulphation method) as it may be distributed on a building would be more useful to assess damage on materials than a similar survey showing distribution of concentration of pollutants because the deposition velocity would be unknown.

6.7.1.2 IRMA Method

A method involving the IRMA (Immission Rate Monitoring Apparatus) monitoring instrument has been used by a number of workers including Luckat (1977), who studied the stone deterioration on Cologne Cathedral. This method measures the flux of SO₂. This work shows an increase in the flux with height ranging from a low of 62.6 at 20 m to a high of 125 mg.m⁻².d⁻¹ at 100 m height. Luckat's data also show about a 3-fold increase in winter values from those obtained in the summer due to high concentration and high time-of-wetness in the winter even though the velocity of deposition is probably lower. These data are much more meaningful than concentration data. However, they should be supplemented by measurement of the time-of-wetness as discussed in previous sections.

6.7.1.3 Analysis of Stone

The most direct method to monitor the flux of SO₂ deposition on stone involves the sampling of the stone on a given building and analyzing it for sulfur content as was carried out by Furlan and Girardet (1983); Girardet and Furlan (1982); and Luckat (1981). This work enabled values of flux to be derived for sandstone at a number of sites in Germany ranging from 0.7 to 12.5 g/m²/year. This work showed that "dry" deposition contributed from 3 to 7 times more sulfur than "wet" deposition. The values for flux obtained by this method were lower than those obtained using IRMA method, which provides a wet surface.

6.7.1.4 XPS Method

A recent study by Garbassi and Mello (1985) reports on an in-situ method for monitoring SO_2 and NO_x flux by the use of XPS (X-Ray Photoelectron Spectroscopy). Samples of Carrara marble (similar to the stone used in the structure) were placed at two elevations, 4 m and 30 m, on the Colonna Antonina, Piazza Colonna in Rome for these measurements. The concentration of SO_2 and NO_x were also monitored at the same locations.

6.7.2 Wet Deposition

A number of studies on stone deterioration included analyses of rainwater and water collected after draining from stone surfaces, in order to account for the deterioration caused by wet deposition (Flinn et al 1985; Livingston et al 1984) but at this time, there is some doubt in the author's mind that such measurements are useful. Not only does dry (gaseous) deposition appear to be much more important but also there is much evidence that aerosol (fog) droplets can acquire high concentrations of acidic constituents having a pH as low as 2.0 and can be deposited as "dry" deposition.

6.7.2.1 Wetting of Materials on Buildings by Rain

Although rain has been viewed as "wet" deposition of pollutants, it now appears that rain may even have a beneficial function of removing some of the acidic constituents deposited by "dry" deposition. Certainly this action was observed on aluminium cladding (Kucera 1978). Where staining of surfaces occurs, rainwater draining over the surfaces in an irregular manner is involved. Much documentation exists to show that deterioration of stone is very different in areas washed by rain than in areas sheltered from rain. In view of these observations it would be advisable to monitor the wetting profiles on buildings where effects of acid deposition are being studied (Robinson and Baker, 1975).

6.8 RESEARCH NEEDS

This update review has led the writer to the conclusion that the state-of-the-art presents an indefinite picture of the processes of corrosion and deterioration regarding effects of acid deposition on materials. It is clear that the mechanisms involved are poorly understood at best, and very little of the recorded data of damage to materials can be definitely linked to acid deposition. Many reported studies of apparent damage to materials do not provide any evidence of levels of pollution.

There is need to undertake coordinated laboratory and field studies involving competent materials scientists in cooperation with experts in monitoring pollution and microclimatic factors. Such studies should be able to resolve mechanisms of failure and quantify the contribution of acid deposition.

6.8.1 What Testing is Required?

Laboratory and field testing with small standard samples in a uniform manner has shown the complexity of reactions and microclimatic effects involved in corrosion and deterioration processes. This complexity is compounded when materials are exposed on buildings so that direct application of data obtained by such laboratory and field testing with standard samples is not possible.

Recommendation: A network of suitable buildings, located in all the major cities across Canada, should be selected to serve as sites for monitoring levels of pollution and microclimatic factors. Such a monitoring program must be coordinated with characterization and monitoring of material damage. Laboratory studies coordinated with field studies are a necessity.

6.8.1.1 Recommendation for Monitoring the Distribution of the Time-of-Wetness

Time-of-wetness is a very important microclimatic factor that must be quantified if damage to materials is to be accounted. Although various devices have been developed for monitoring the time-of-wetness, that developed by N.R.C. (Sereda et al. 1980) and for which there is an ASTM Standard (ASTM 6-84, 1984), appears most logical for use to determine the distribution of this parameter on an existing building. A system to monitor the time-of-wetness on a building has been proposed by April et al. (1986). Kung (1986) has instrumented a brick building to monitor degree of saturation by using similar sensors imbedded in bricks located on the various parts of the building. Jerovsky et al. (1982) describe a sensor for measuring the time-of-wetness that is used in Czechoslovakia. Flinn et al. (1985) are using the sensors developed at NRC in their NAPAP program. Dassu et al. (1985) report on studies to monitor climate and microclimate data on a historic building.

6.8.1.2 Recommendation for Monitoring the Distribution of Pollutants Deposition Flux

Although SO_2 , NO_x , O_3 , and particulate matter are identified as the precursors that can contribute to material damage, the most important one of these is SO_2 . Most of the available data on pollution levels is given as concentration at ground level. These values by themselves are not adequate because they do not provide the value of flux as discussed previously. Furthermore there are no values given to indicate the distribution with height and location on buildings. Future research must address these requirements.

This review of current literature leads to the conclusion that the most desirable monitoring device would be a passive monitor (dosimeter) that would provide an integrating value for the flux that incorporates a reactive surface and accounts for microclimatic effects of surface condensation and wind. The sulphation plates and the nitration plates meet most of the above criteria and have the advantage of long use with

the corresponding background of experience. They have the advantage of being a commercial item, but having a disadvantage because all monitoring networks such as NAPS are committed to monitoring the concentration of pollutants in the air.

The IRMA (Immission Rate Monitoring Apparatus) (Luckat, 1972) a German development appears to show promise and has been on trial by Livingston et al. (1981), and is to be evaluated by Flinn et al. (1985) in the NAPAP program. This method, although designed to provide a value of total flux, has the disadvantage that it does not simulate the moisture conditions at the surface of the materials because it provides a continuously wetted surface as well as a totally reactive surface of NaOH solution. Despite its weaknesses, this method deserves further trials. Survey of cumulative flux of sulphates, nitrates and chlorides on porous materials, especially stone in buildings (Luckat, 1977) should be carried out to indicate the rate of deposition that has taken place in the life of the building.

Passive dosimeter type of monitoring devices such as sulphation plates or IRMA provide a highly "reactive" surface to foster complete absorption of the pollutant molecules (high deposition velocity). Whereas this may simulate certain material surfaces when they are wet, it is not likely to simulate the "reactivity" of different material surfaces when dry. Research is needed to establish the calibration factors to arrive at values of flux for a variety of practical materials (to take into account the different chemical and physical characteristics) from values of flux obtained by the sulphation plates or the IRMA.

6.8.1.3 Recommendation for Monitoring the Distribution of Chloride Deposition

Chloride deposition is a special case representing both the man-made source and a natural source. In coastal areas, in close proximity to the sea, chloride deposition must be monitored because its contribution can mask that of acid deposition. The man-made source of de-icing salts can be particularly damaging to steel reinforcing in concrete on bridges and parking garages and should be properly identified and not confused with effects of acid deposition.

6.8.2 Materials at Risk

Materials in service on structures are subject to a variety of corrosion and deterioration processes including effects of acid deposition. Even those that are damaged predominantly by acid deposition are subject to different severity of attack on a structure because of variation in deposition rates and microclimatic conditions including time-of-wetness, wetting by rain, temperature, U.V. irradiation and others. Therefore, materials on structures experience different degrees of risk.

6.8.2.1 What is the State of Materials on Buildings?

Surveys of the extent of deterioration and corrosion of selected classes of materials on buildings should be undertaken coupled with statistics of life-cycle performance and maintenance costs. Such survey should establish a ranking for the degree of risk that various materials experience. This would provide a necessary data base that should establish the priority for future research and ensure the maximum cost benefit.

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